Basic Principles and Calculations in Chemical Engineering
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Lecture - 26
Energy Balance with Heat of Combustion

Welcome to massive open online course on Basic Principles and Calculations in Chemical Engineering. So we were discussing energy balances on reactive systems with examples. So in this lecture we will try to discuss about the energy balance with heat of combustion with some examples.

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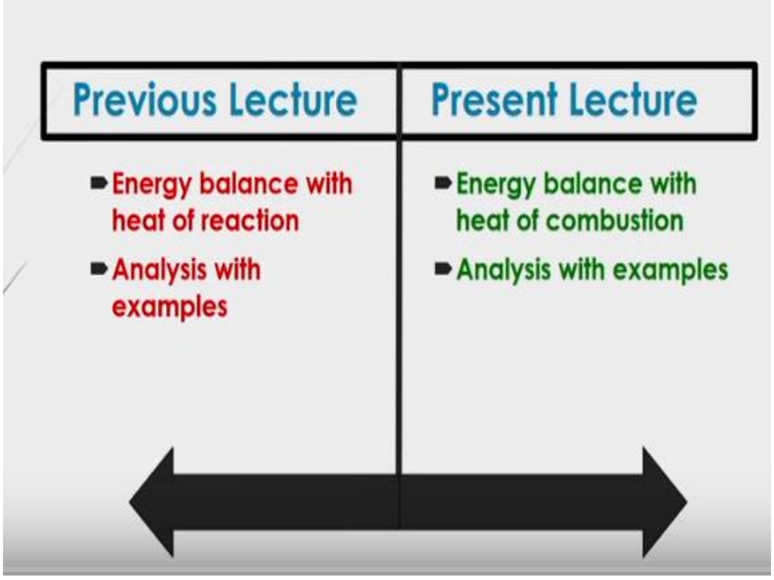

Previous Lecture	Present Lecture
Energy balance with heat of reaction	Energy balance with heat of combustion
Analysis with examples	Analysis with examples

In the previous lectures we have described the energy balance with heat of reaction and analysis with different examples. Now previous lecture, we have given that equation for calculating that heat of formation from the heat of reaction that is experimentally obtained for the case where there will be no phase change.

Also, we have described the heat of reaction based on you know heat of formation for the compounds which are taking part in particular reactions. We have also you know described about the heat of reaction, how it can be calculated based on their operating condition in a particular systems.

That means when temperature is changing from reference temperature to a certain temperature, how to calculate that heat of reaction that we have given and that heat of reaction to be actually calculated based on the you know heat of formation of reactant and products components also sensible heat change for that reactants and products for changing the temperature as a sensible heat.

And then along with this differences in enthalpies you have to you know add that heat of reaction at standard condition.

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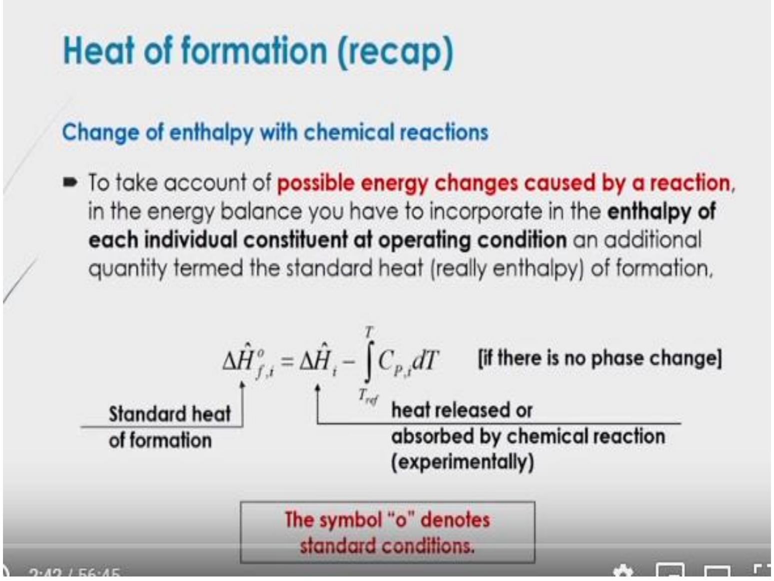

Heat of formation (recap)

Change of enthalpy with chemical reactions

- To take account of **possible energy changes caused by a reaction**, in the energy balance you have to incorporate in the **enthalpy of each individual constituent at operating condition** an additional quantity termed the standard heat (really enthalpy) of formation,

$$\Delta \hat{H}^o_{f,i} = \Delta \hat{H}_i - \int_{T_{ref}}^{T} C_{P,i} \, dT$$

[if there is no phase change]

Standard heat of formation

heat released or absorbed by chemical reaction (experimentally)

The symbol "o" denotes standard conditions.

So based on these principles we have already described all these things and analyzed based on different experiments and different examples there in the previous lecture.

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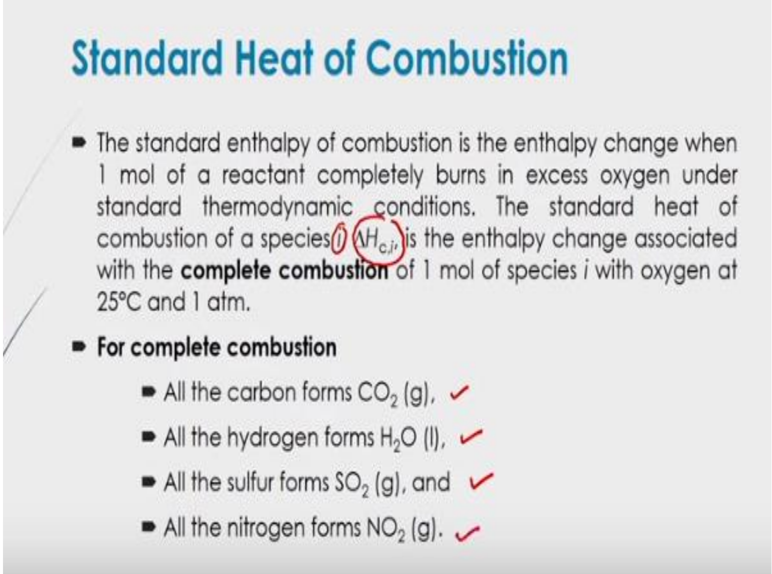

Standard Heat of Combustion

- The standard enthalpy of combustion is the enthalpy change when 1 mol of a reactant completely burns in excess oxygen under standard thermodynamic conditions. The standard heat of combustion of a species (*i*) ($\Delta H_{c,i}$) is the enthalpy change associated with the **complete combustion** of 1 mol of species *i* with oxygen at 25°C and 1 atm.
- **For complete combustion**
  - All the carbon forms CO_2 (g). ✓
  - All the hydrogen forms H_2O (l). ✓
  - All the sulfur forms SO_2 (g), and ✓
  - All the nitrogen forms NO_2 (g). ✓

In this lecture we will try to discuss about that standard heat of combustion. You know that there are several combustion reactions are there to you know, you know obtain the products as you know carbon dioxide, carbon monoxide along with valuable products after combustion. So in that case, how to calculate that standard heat of combustion there at a standard condition.

Now this is basically the enthalpy change when one mole of reactant completely burns in excess of oxygen under standard thermodynamic conditions and the standard heat of combustion of the species suppose if there is a species i,

So we can say that this standard heat of combustion can be you know represented by this delta H c i will be the enthalpy change which will be associated with the complete combustion of one mole of species i with oxygen at standard condition of 25 degrees Celsius and one atmosphere. Now what is the complete combustion actually?

For complete combustion, you will see that there will be a conversion of all carbons into a carbon dioxide gas and all the hydrogen that is in the you know main components which is to be combust which is to be burnt will be converted into you know water.

And all the sulfur if it is there in the you know, feed components which are actually to be burned, it will be you know converted to sulfur dioxide after complete combustion. And all the nitrogen similarly, will forms nitrogen dioxide. So in this way, you can say that when there will be a complete combustion of any you know compounds then you will see that what should be the heat of combustion and how to calculate there.

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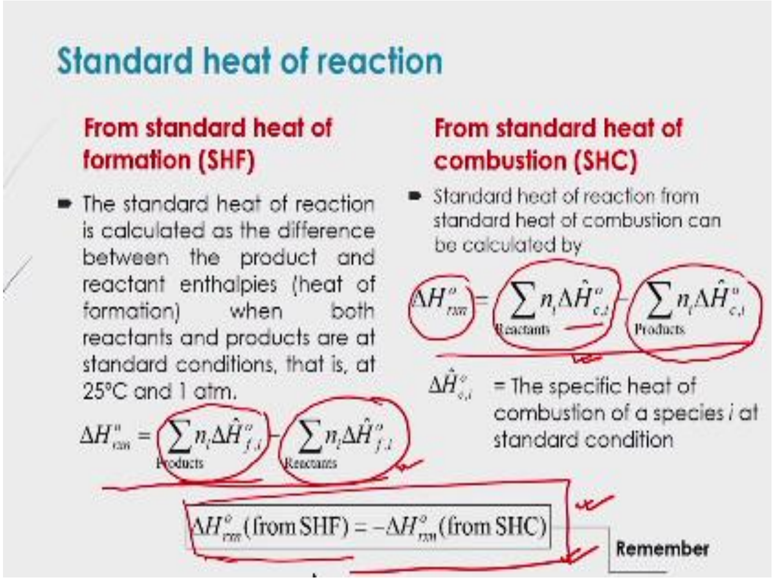

Standard heat of reaction

From standard heat of formation (SHF)

- The standard heat of reaction is calculated as the difference between the product and reactant enthalpies (heat of formation) when both reactants and products are at standard conditions, that is, at 25°C and 1 atm.

$$\Delta H^o_{rxn} = \sum_{\text{Products}} n_i \Delta \hat{H}^o_{f,i} - \sum_{\text{Reactants}} n_i \Delta \hat{H}^o_{f,i}$$

From standard heat of combustion (SHC)

- Standard heat of reaction from standard heat of combustion can be calculated by

$$\Delta H^o_{rxn} = \sum_{\text{Reactants}} n_i \Delta \hat{H}^o_{c,i} - \sum_{\text{Products}} n_i \Delta \hat{H}^o_{c,i}$$

$\Delta \hat{H}^o_{c,i}$ = The specific heat of combustion of a species *i* at standard condition

$$\boxed{\Delta H^o_{rxn}(\text{from SHF}) = -\Delta H^o_{rxn}(\text{from SHC})}$$

Remember

As we know that standard heat of reaction that is actually obtained based on that heat of you know formation of that constituents, which are taking part in the particular reactions.

So in that case we have described that standard heat of reaction is calculated as the difference between the product and reactant enthalpies that is heat of formation where both reactants and products are at standard conditions that is at 25 degrees Celsius and one atmosphere. So according to that, you know principles we are actually calculating that standard heat of reaction by this equation.

Here, standard heat of formation for all products components and standard heat of formation for all reactant components and subtracting that will give you the standard heat of reaction. Now standard heat of combustion can be actually again that estimated or calculated from the standard heat of combustion and based on this you know reaction.

So here standard heat of reaction that is here can be calculated here like this here if you know that reactants components which are taking part in the reactions. Now for those components what should be the standard heat of combustions there and then the standard heat of combustions for that reactants, what will be the total amount of that enthalpy change because of that combustion for that constituents in reactants.

Similarly, what will be the total amount of enthalpy change for the constituents of products when you know that, that specific enthalpy of combustion is there. So from this actually, you can calculate that heat of reaction from the you know standard heat of combustion.

So this is basically the same way, how you are calculating the standard heat of reaction from the standard heat of formation. Here also that same way same fashion, that you can calculate the standard heat of reaction from the standard heat of combustion of the constituents. But in this case, you have to remember that, you are going to subtract this you know that enthalpy change from the reactants of you know there.

But whereas, the standard heat of reaction whenever you are calculating from the standard heat of formation there you are subtracting the you know standard heat of you know formation of that reactants from the you know product side.

So basically here we can say that standard heat of reaction will be is equal to negative of standard heat of reaction from the standard heat of combustion. So from this you know equation you can easily calculate what should be the standard heat of reaction from standard heat of combustion there.

So you have to remember this format. Only thing is that you have to know what should be the standard heat of combustion for individual components or individual constituents of that reaction there. So simple way to calculate that standard heat of reaction from the standard heat of combustion.

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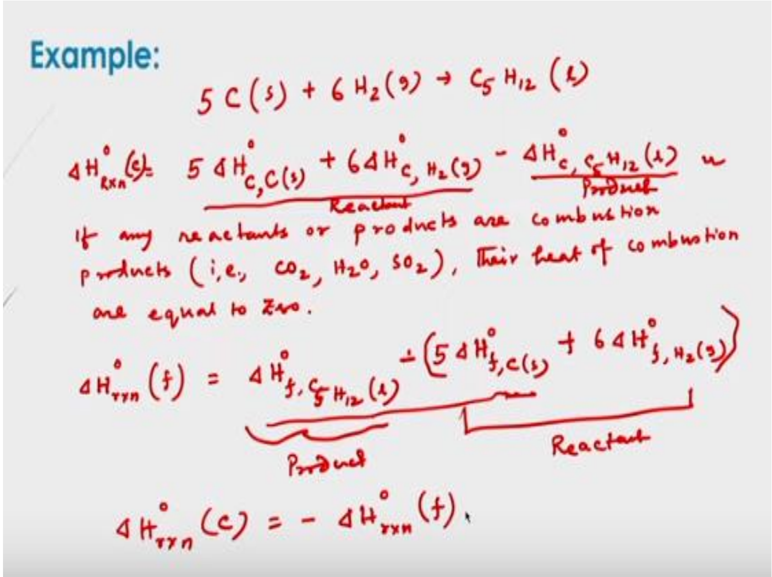

Example:

$$5C(s) + 6H_2(g) \rightarrow C_5H_{12}(l)$$

$$\Delta H^{\circ}_{Rxn}(c) = \underbrace{5\Delta H^{\circ}_{c,C(s)} + 6\Delta H^{\circ}_{c,H_2(g)}}_{Reactant} - \underbrace{\Delta H^{\circ}_{c,C_5H_{12}(l)}}_{Product}$$

If any reactants or products are combustion products (i.e., CO_2, H_2O, SO_2), their heat of combustion are equal to zero.

$$\Delta H^{\circ}_{rxn}(f) = \underbrace{\Delta H^{\circ}_{f,C_5H_{12}(l)}}_{Product} - \underbrace{\left(5\Delta H^{\circ}_{f,C(s)} + 6\Delta H^{\circ}_{f,H_2(g)}\right)}_{Reactant}$$

$$\Delta H^{\circ}_{rxn}(c) = -\Delta H^{\circ}_{rxn}(f).$$

So let us do an example here like carbon, solid carbon is you know reacting with you know, a hydrogen gas, which will give you that C 5 H 12 here as liquid. Now from this reaction, we can say that carbon, hydrogen and pentane you know can all be burned and their standard heat of combustion can be you know determined experimentally.

Now the standard heat of you know reaction from that standard heat of combustion can be then calculated here. So delta H you know Rxn at standard condition that will be is equal to here what will be the in this case here reactants minus you know products that you have to remember here.

So 5 into you know standard heat of you know combustion. For combustion we are writing c, whereas for formation we are writing f. So delta H c here at standard condition for the constituents here reactants is c that is carbon as here solid and plus other constituents in the reactant side is hydrogen.

So your stoichiometric coefficient is here 6, so 6 into delta H here of combustion of hydrogen gas at the standard condition minus what will be the standard heat of you know combustion for this you know product of this pentane that is C 5 H 12 in liquid form.

So from this you know equation you can calculate what will be the standard heat of reaction from this standard heat of combination of all these constituents. Now if any reactants, suppose if any reactants or products are combustion products**.** Let us have example here.

Like suppose carbon dioxide, water, sulfur dioxide, then their heat of combustion, are equal to zero**.** As what we have discussed earlier also for naturally you know existing any gas or substances you will see that heat of formation will be equals to zero.

Similarly, here also we can say that this you know products of combustion here like carbon dioxide, water and sulfur dioxide all will have their you know heat of combustion will be equals to zero. Now the standard heat of formation as like this here according to this here c instead of c it will be coming as f there.

But here you will see that standard you know heat of reaction in this case here we are considering first reactants and products. And but standard heat of reaction in that case in case of you know that formation, we have to write it in just negative of this heat of reaction by combustion here.

So if we represent it as per combustion, so we can write here standard heat of reaction of as for you know formation f, so we can write here this s you know that delta H here f instead of c. Here product side will come first.

Then it will be C 5 H 12 as liquid, then minus it will be 5 into delta H formation of this you know carbon solid minus here 6 into delta H at standard condition for this formation of this you know hydrogen gas there. So in this way we can calculate. So here this is basically the you know reactant and here this is product for standard heat of reaction from combustion.

But here in this case, it is you know that this will be this, this is actually this one will be you know that product where this to this will be your, you know reactant. You can subtract it here like this also. Here in this way also you can represent. So this is the you know standard heat of reaction which are obtained from heat of combustion and heat of formation.

And how they are related? Simply since here delta H rxn this is combustion, we will be is equal to negative of delta H. Here rxn that is reaction at standard condition based on standard heat of formation, okay.

Next, we will do another you know example for this like here suppose you have to calculate the standard heat of reaction as follows from the standard heat of formation and standard heat of combustion for this you know reaction given in the slide.

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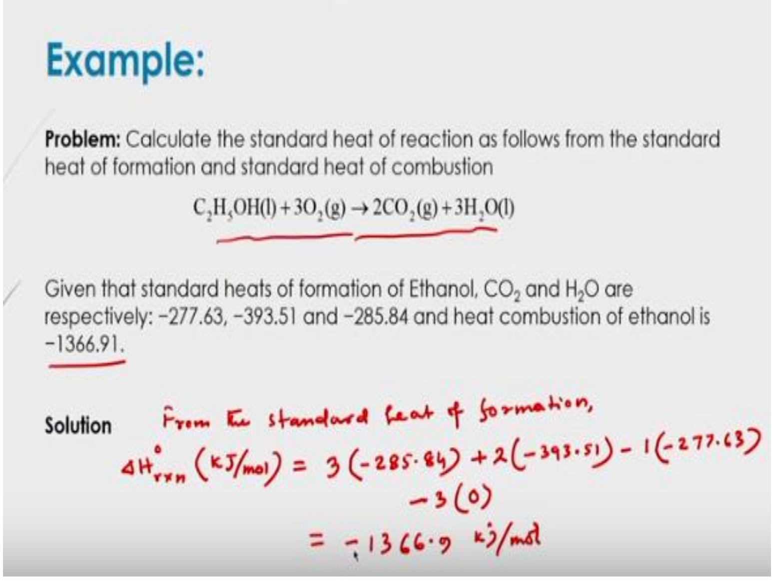

Example:

Problem: Calculate the standard heat of reaction as follows from the standard heat of formation and standard heat of combustion

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

Given that standard heats of formation of Ethanol, CO_2 and H_2O are respectively: −277.63, −393.51 and −285.84 and heat combustion of ethanol is −1366.91.

Solution From the standard heat of formation,

$$\Delta H^{\circ}_{rxn}\,(kJ/mol) = 3(-285.84) + 2(-393.51) - 1(-277.63) - 3(0)$$

$$= -1366.9 \text{ kJ/mol}$$

In this case ethanol will be you know reacting with oxygen which will give you that carbon dioxide and water after complete combustion. Now in this case the heat of formation of ethanol, carbon dioxide and water are respectively given as -277.63, -393.51 and -285.84. And heat of combustion of ethanol is given as -1366.91.

So based on this you have to calculate what will be the standard heat of reaction based on this standard heat of formation. Since it is you know that combustion reaction so first of all we have to find out what will be the standard heat of reaction based on this value given for standard heat of formation of all constituents here for the reactants and product sides.

So as a solution we can write here we can first calculate that from the standard heat of formation, from the standard heat of formation we can write delta H rxn at standard condition in kilojoule per, it is given kilojoule per mole. That will be is equal to here what should be the first we have to consider here product side.

The for the product side we can write here this 3 into for water what is the standard heat of formation it is given. This is -285.84 plus here 2 into for carbon dioxide it is given -393.51. Then minus in your reactant side or specific heat of you know that standard condition of heat of formation for those components are like this.

So accordingly what is the stoichiometric component or coefficient for this reactant side here. For ethanol it is one. So we can write one into for ethanol this standard heat of formation is given -277.63 and then minus the stoichiometric coefficient of oxygen, it is 3. So 3 into what is the specific heat of combustion at standard condition for oxygen it is given or not.

It is not since it is a naturally occurring compound, so you have to consider it as zero. So finally, we can get after you know calculation then you can have this -1366.9 kilojoule per mole. So in this way, you can calculate what will be the standard heat of you know reaction based on the standard heat of formation.

Similarly, we can then calculate the standard heat of combustion from the you know reaction as like this.

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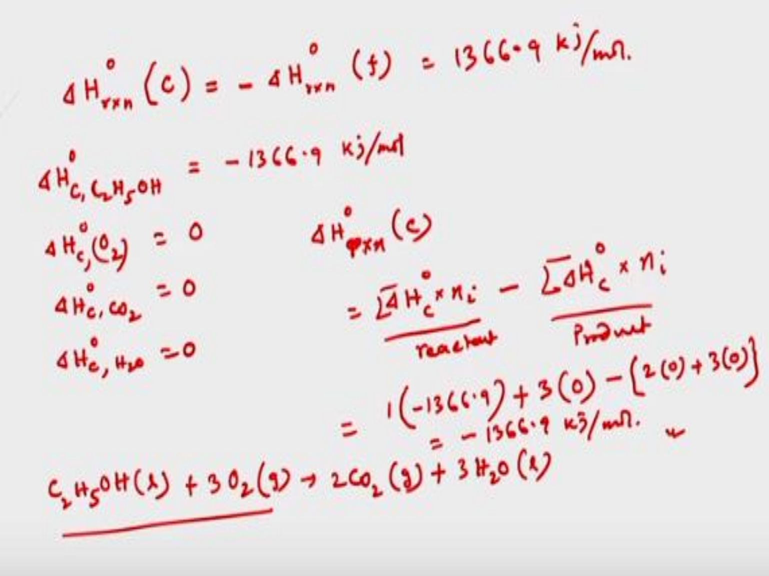

$$\Delta H^{o}_{rxn}(c) = -\Delta H^{o}_{rxn}(f) = 1366.9\ kJ/mol.$$

$$\Delta H^{o}_{c, C_2H_5OH} = -1366.9\ kJ/mol$$

$$\Delta H^{o}_{c}(O_2) = 0$$

$$\Delta H^{o}_{c, CO_2} = 0$$

$$\Delta H^{o}_{c, H_2O} = 0$$

$$\Delta H^{o}_{rxn}(c) = \underbrace{\sum \Delta H^{o}_{c} \times n_i}_{\text{reactant}} - \underbrace{\sum \Delta H^{o}_{c} \times n_i}_{\text{Product}}$$

$$= 1(-1366.9) + 3(0) - \{2(0) + 3(0)\}$$

$$= -1366.9\ kJ/mol.$$

$$\underline{C_2H_5OH(l) + 3O_2(g)} \rightarrow 2CO_2(g) + 3H_2O(l)$$

Here in this case the standard heat of reaction for combustion that will be is equal to what negative of you know that delta H you know that rxn at standard condition of formation. So like this you can get it or otherwise you can get the standard heat of you know combustion based on the standard heat of you know combustion of individual constituents.

Now if we consider that standard heat of actually combustion for ethanol delta H you know combustion at standard condition for C 2 H 5 OH. This is basically you know -1366.9 kilojoule per mole. And also you can say that standard heat of combustion for other components in this reaction here delta H c of degree here oxygen since it is naturally occurring substance this will be equal to zero.

Similarly delta H c for you know carbon dioxide it will be 0. Similarly, delta H c that will be for water, that also zero. So based on the you know formula for standard heat of combustion reaction, So delta H c of reaction that is you know that we can say here rxn for combustion, that will be is equal to here delta H summation of delta H of combustion into in i minus, this is in product side.

Sorry this is reactant side, reactant and minus summation of delta H c standard heat of the combustion into you know n i. This is actually for product side. So based on these we can say that since here we are getting these reactant or like you know that methanol. Okay let us write this equation first. C 2 H 5 OH that is liquid plus 3 oxygen that is gas that will give you to 2 CO 2 here gas plus 3 water, liquid.

Now in this case what are the reactant side? These are the reactant side. So according we can write here, it will be basically number of moles of that ethanol is according to this reaction is one. So it will be here and standard heat of condition for this ethanol is given to you. This is -1366.9 and then plus other components here.

Then 3 into oxygen here it is zero minus here it will be, what is that combustion for product side. This is 2 into then carbon dioxide here again zero plus here 3 into for water it is zero. So here we can say finally after simplification, it will be coming as -1366.9 you know kilojoule per mole. So this one in this way you can you know calculate the standard heat of reaction based on the combustion reaction.

But since we have calculated earlier the standard heat of formation and its value was here minus you know 1366.9. So accordingly we can say that this value will be coming as here standard heat of combustion will be is equal to this simply here again the 1366.9 kilojoule per mole.

So you can say here in this way you can simply calculate what should be that standard heat of combustion and standard heat of formation based standard heat of reaction. So both are, in both cases we are we are having the same results for standard heat of reaction.

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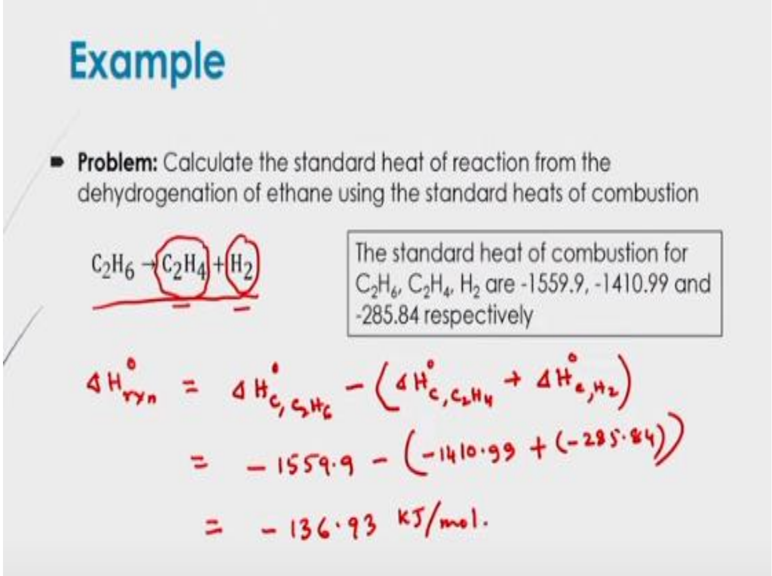

Example

- **Problem:** Calculate the standard heat of reaction from the dehydrogenation of ethane using the standard heats of combustion

$C_2H_6 \rightarrow C_2H_4 + H_2$

The standard heat of combustion for C_2H_6, C_2H_4, H_2 are -1559.9, -1410.99 and -285.84 respectively

$$\Delta H^\circ_{ryn} = \Delta H^\circ_{c,C_2H_6} - \left(\Delta H^\circ_{c,C_2H_4} + \Delta H^\circ_{c,H_2}\right)$$

$$= -1559.9 - \left(-1410.99 + (-285.84)\right)$$

$$= -136.93 \text{ KJ/mol.}$$

Let us do another example. In this case, calculate the standard heat of reaction from the you know dehydrogenation of ethane using the standard heat of combustion. This reaction is given to you here in this case dehydrogenation of ethane giving you that here ethane and hydrogen.

Now standard heat of combustion for this you know ethane and ethane is given to you, ethylene is given to you and hydrogen also is given to you. So ethane is given to ethylene and hydrogen gas and their respective heat of combustions are given like this. So based on this you know standard heat of combustion you have to calculate what will be the standard heat of reaction.

So again you can then write the same principle of calculating standard heat of reaction for this combustion reaction. It will be is equal to delta H c for this you know ethane C 2 H 6 and this is your you know reactants minus here it will be delta H you know combustion at standard condition for ethylene C 2 H 4 plus here delta H here combustion for you know hydrogen gas.

So in this case if we substitute the value of this standard you know heat of combustion for its constituents, then you can right here, this will be is equal to minus here 1559.9, this is for ethane, minus here for ethylene it is given -1410.99 and plus here for hydrogen it is given -285.84 like this.

So after calculation, we can have this heat of reaction as -136.93 kilojoule per mole. So in this way you can calculate what will be the standard heat of reaction based on the standard heat of combustion, okay. And then we can have another example for this.

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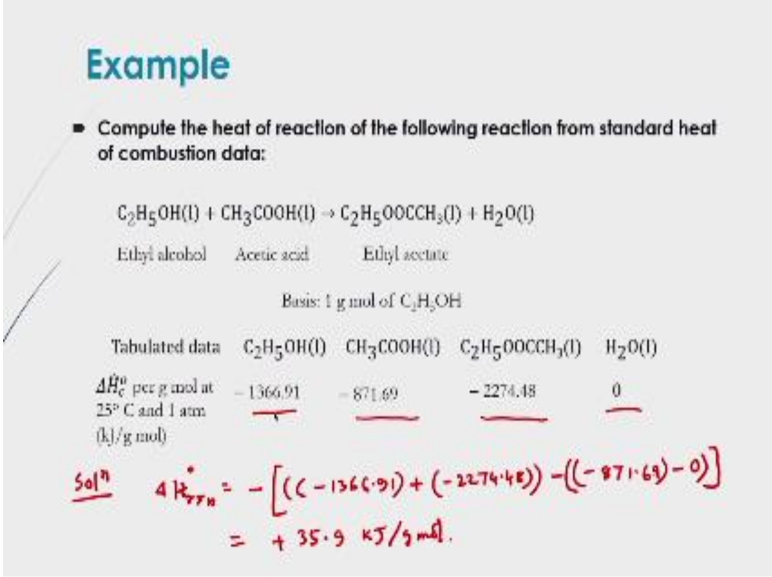

Example

- Compute the heat of reaction of the following reaction from standard heat of combustion data:

$$C_2H_5OH(l) + CH_3COOH(l) \rightarrow C_2H_5OOCCH_3(l) + H_2O(l)$$

Ethyl alcohol Acetic acid Ethyl acetate

Basis: 1 g mol of C_2H_5OH

Tabulated data	$C_2H_5OH(l)$	$CH_3COOH(l)$	$C_2H_5OOCCH_3(l)$	$H_2O(l)$
$\Delta\hat{H}^{o}_{c}$ per g mol at 25° C and 1 atm (kJ/g mol)	−1366.91	−871.69	−2274.48	0

Sol^n $\Delta\hat{H}^{\circ}_{rxn} = -[((-1366.91)+(-2274.48)) - ((-871.69)-0)]$

$= +35.9$ KJ/gmol.

Like you have to calculate the heat of reaction of the following reaction from the standard heat of combustion data. Here ethyl alcohol will be you know, reacting with acetic acid which will give you that ethyl acetate and water. In this case one gram mole of ethanol is considered.

And based on this your standard heat of combustion for each components at 25 degree Celsius and one atmospheric condition is given as for ethanol it is given. For acetic acid also it is given. Here ethyl acetate is given. For water it will be zero of course. So based on this example, how to calculate the you know standard you know heat of combustion.

So here again as per same principles you can you know calculate this as here then standard heat of reaction that will be is equal to here as per combustion, it will be is equal to what this minus of this is you can say that minus here 1366.91. This is for reactants and plus here -2274.48. Here this is your reactant side.

And then minus of minus you know that 871.69. Then here you can say that minus of again 0 for water and we can say that here within a bracket and then finally, third bracket closed. So after substitution of this, you know constituents value in the reactants and product side.

And finally we can get after calculation it will be coming as positive of 35.9 kilojoule per gram mole. So in this way you can have this value of heat of reaction from this standard heat of combustion.

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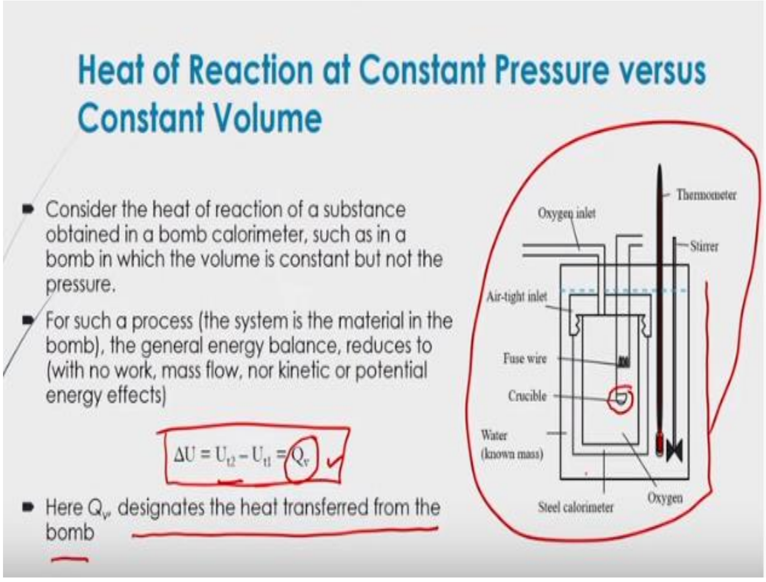

Heat of Reaction at Constant Pressure versus Constant Volume

- Consider the heat of reaction of a substance obtained in a bomb calorimeter, such as in a bomb in which the volume is constant but not the pressure.
- For such a process (the system is the material in the bomb), the general energy balance, reduces to (with no work, mass flow, nor kinetic or potential energy effects)

$$\boxed{\Delta U = U_{t2} - U_{t1} = Q_v}$$

- Here Q_v designates the heat transferred from the bomb

Now we will discuss about that heat of reaction at constant pressure versus constant volume. In this case whatever you know condition for standard heat of reaction, standard heat of combustion, that will be a certain you know pressure and certain volume there.

If it is suppose closed vessel or if it is open condition or open vessel system, open process unit system there accordingly how to calculate that standard heat of reaction, standard heat of you know formation, standard heat of you know combustion, that we have described. And also based on that you know operating condition how to calculate the standard heat of reaction based on the standard heat of formation.

Even a standard not only the standard condition you can calculate heat of reaction at other operating conditions also if there is a temperature change. So based on which we have calculated also, because of that sensible heat change by you know temperature change.

Now the condition is that in this case what should be the standard heat of reaction at constant pressure and also what should the standard you know heat of reaction or heat of reaction at constant volume. Now sometimes this will be you know applied for a certain you know, chemical engineering operation like for you know proximate analysis.

Or some other analysis of you know particles in a closed system at constant temperature and also constant you know volume, constant pressure. So how to find out that heat of reaction when it is done in a closed you know volume at a constant volume and at a constant pressure there.

Now considered the heat of reaction of a substance that is you know obtained in a bomb calorimeter. It is basically you know that a constant volume system, but there pressure is not keeping constant and it is a closed vessel where there will be a certain you know, combustion reaction is taking place.

Now for such process in this case, material in the bomb as shown in the figure here, see this is a totally you know sealed you know volume here as shown in the diagram. That you will see that inside that you know bomb, there is you know crucible is kept and then in this crucible some solid particles to be burned by you know supplying some heat energy there.

And then also according to that supplying energy and also the you know in presence of oxygen, otherwise the burning will not be there. So oxygen will be you know supplying from inlet of this closed system there. And there will be a airtight sealing of this you know bomb calorimeter system where you know that outside this system some you know water to be there.

And a certain temperature to be maintained in that water bath. And based on that at constant temperature and constant volume what should be the heat of you know reaction that you have to find out by this bomb calorimeter. Now for such systems then I can say that the general energy balance will be reducing to here you know delta U that is total you know internal energy change that will be is equal to U t 2 – U t 1.

Here at a certain time interval this you know reactions will be you know allowed to do there. So in that case total heat energy will be changed between during this time interval and as per that general energy balance equation. Of course some other terms will be there like shaft work, even here also kinetic energy, potential energy will be there.

Since it is a closed vessel, there will be no flow of the you know materials there and also there will be no energy or work done on this system externally by any you know pump or some other you know, mechanical device. So in that case we can consider that there will be no work done there and there will mass flow rate also here since it is a batch wise process.

And there is no kinetic energy change because there is no flow and there is no potential energy effect also because this crucible is you know or material is kept at a certain position and there will be no you know positional effect and gravitational effect on that at a particular position there.

So ultimately we can say that neglecting all other that you know shaft work, flow work and kinetic and potential energy terms there. So the final energy balance equation will be giving you like this simple that total internal energy change because of that you know heat supply and changing the temperature inside the bomb with respect to time.

And accordingly what should be the heat energy released there or heat energy you know produced based on this reaction that you have to calculate. So here Q v is basically the heat that is transferred from the bomb at a constant volume.

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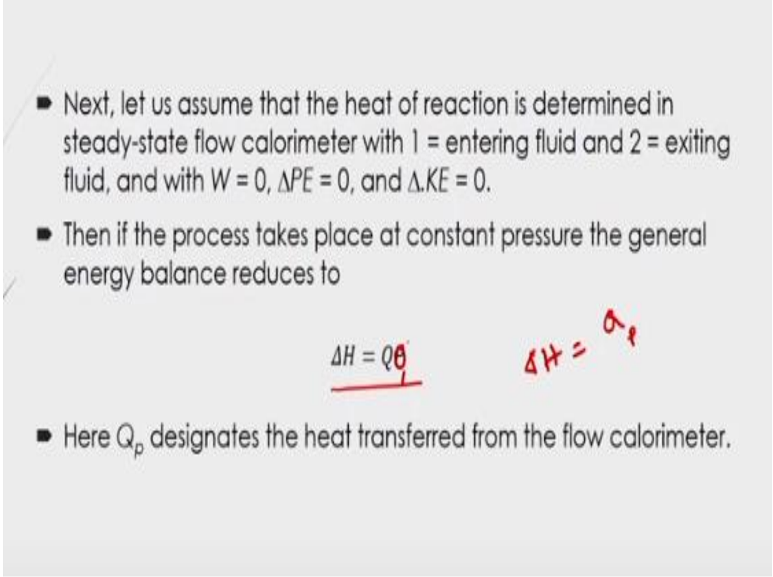

- Next, let us assume that the heat of reaction is determined in steady-state flow calorimeter with 1 = entering fluid and 2 = exiting fluid, and with W = 0, ΔPE = 0, and ΔKE = 0.
- Then if the process takes place at constant pressure the general energy balance reduces to

$$\underline{\Delta H = Q_p} \qquad \Delta H = Q_p$$

- Here Q_p designates the heat transferred from the flow calorimeter.

And then let us assume that the heat of reaction is determined in steady state flow, you know calorimeter with you know entering fluid at position one and the exiting fluid at position two at an open you know process unit system and there if no shaft work is supplied to that system. And if it kept horizontally then potential energy will be negligible.

Or you can see zero and kinetic energy will be also considered as zero there. So in that case, if the process takes place at constant pressure, the general energy balance will be reducing to you know delta H will be is equal to Q p. Here Q p is in suffix. So it is delta H will be is equal to Q p. Here Q p designates you know the heat transferred from the flow calorimeter at a constant pressure.

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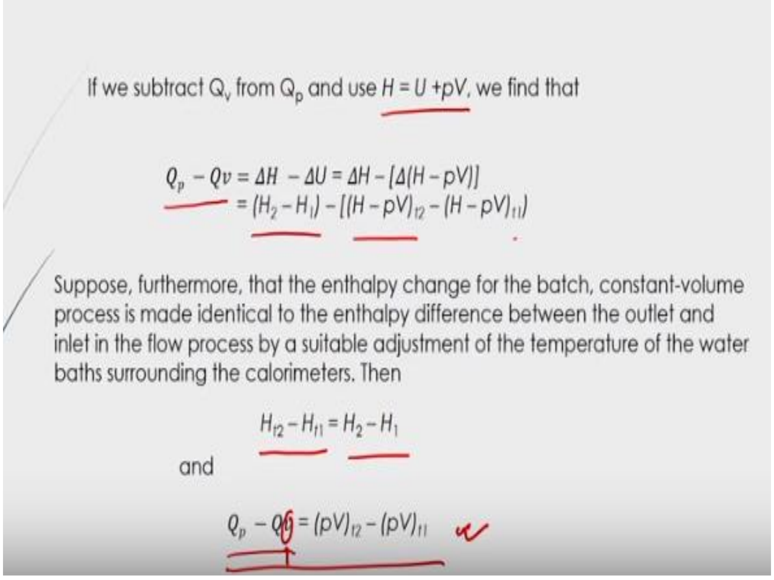

If we subtract Q_v from Q_p and use $H = U + pV$, we find that

$$Q_p - Qv = \Delta H - \Delta U = \Delta H - [\Delta(H - pV)]$$
$$= (H_2 - H_1) - [(H - pV)_{t2} - (H - pV)_{t1})$$

Suppose, furthermore, that the enthalpy change for the batch, constant-volume process is made identical to the enthalpy difference between the outlet and inlet in the flow process by a suitable adjustment of the temperature of the water baths surrounding the calorimeters. Then

$$H_{t2} - H_{t1} = H_2 - H_1$$

and

$$Q_p - Q_v = (pV)_{t2} - (pV)_{t1}$$

Now if we subtract this you know Q v from Q p and use the relationship of enthalpy with this you know internal energy as like this H is equal to U + p V. Then we can find out that what should be the Q p – Q v. That will be is equal to delta H – delta U. This is basically delta H minus delta H minus you know p V.

Now this delta H is basically H 2 – H 1. And that is state 1 to state 2. Similarly, here this flow work from this you know at this you know time two here H – p V and H – p V at this condition of you know t 2 to t 1.

Now furthermore, we can say that the enthalpy change for the you know batch constant volume process is made identical to the enthalpy difference between the outlet and the inlet in the process by a suitable adjustment of the temperature of the water baths, that is surrounded to that you know bomb calorimeter.

So in that case we can say that this H t 2 – H t 1 that will be is equal to H 2 – H 1 if that temperature is kept constant. And again we can write Q p – Q v, this v is in actually suffix which represents this heat at constant volume. So here Q p – Q v will be coming as p V – p V between this interval of t 2 and t 1.

So from this equation, we can calculate from the flow work at condition two to condition one what should the change of you know heat energy based on that constant pressure and constant volume.

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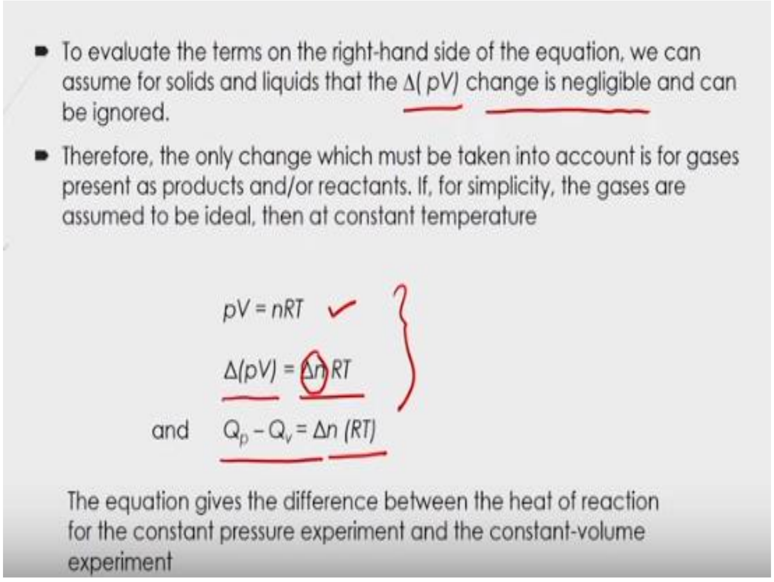

- To evaluate the terms on the right-hand side of the equation, we can assume for solids and liquids that the $\Delta(pV)$ change is negligible and can be ignored.
- Therefore, the only change which must be taken into account is for gases present as products and/or reactants. If, for simplicity, the gases are assumed to be ideal, then at constant temperature

$$pV = nRT$$

$$\Delta(pV) = \Delta n RT$$

and $$Q_p - Q_v = \Delta n (RT)$$

The equation gives the difference between the heat of reaction for the constant pressure experiment and the constant-volume experiment

Now to analyze that right hand side of this you know equation, this flow work. Here in this case, we can assume that for solids and liquids here delta p V change is negligible and can be ignored there. So for such cases, the only change which will be taken into account is for gases that is present as product and or reactants.

And if for simplicity the gases are, you know assumed to be ideal, then at constant temperature we can write this p V will be is equal to nRT and then what will be that gradient of that p V that will be basically based on that gradient of what is that moles there. So it is represented by delta n.

So delta p V will be is equal to delta n into RT where this temperature is kept constant and R is universal gas constant. So based on this you know equation, we can write that Q p – Q v that means change of heat energy based on constant pressure and constant volume, we can write simply delta n into RT.

Now this equation will give you the difference between the heat of reaction for the constant pressure experiment and the constant volume experiment.

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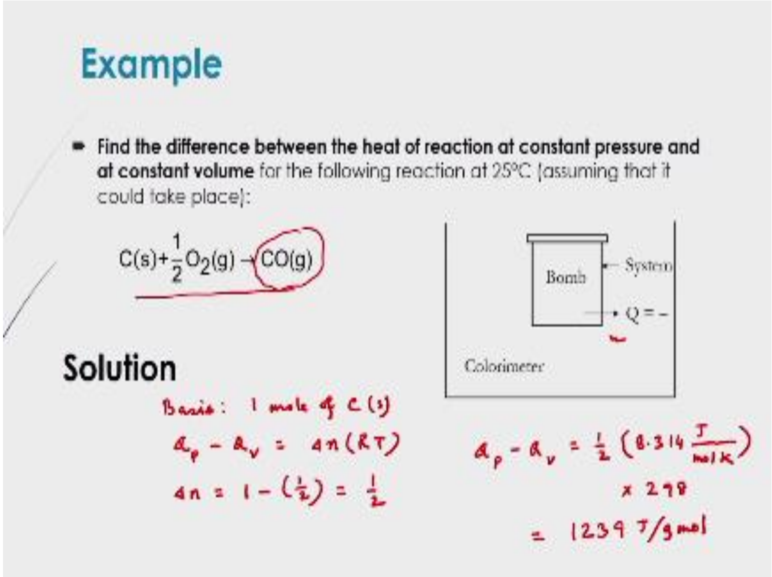

Example

- **Find the difference between the heat of reaction at constant pressure and at constant volume** for the following reaction at 25°C (assuming that it could take place):

$$C(s)+\frac{1}{2}O_2(g)\rightarrow \boxed{CO(g)}$$

Solution

Basis: 1 mole of C (s)

$$Q_p - Q_v = \Delta n\,(RT)$$

$$\Delta n = 1-\left(\frac{1}{2}\right) = \frac{1}{2}$$

$$Q_p - Q_v = \frac{1}{2}\left(8.314\,\frac{J}{mol\,K}\right) \times 298$$

$$= 1239\ J/g\,mol$$

Now let us do an example for such cases. Here in this case, you have to find out what should be the you know the difference between the heat of reaction at constant pressure and constant volume for the following reaction at 25 degree Celsius assuming that it could take place here as per reactions here.

This carbon particles will be bond with oxygen, which will give you that product as carbon monoxide in the bomb calorimeter. So in this case how to calculate this first heat of reaction at constant pressure and constant volume that you have to calculate. In this case, let us consider the basis as one mole of carbon solid.

So as par the figure here the you know system is bomb here and Q let us see what will be that Q value. It should be positive since it is you know absorbed by the bomb. And we can say that from the equation like Q p – Q v we know that this is delta n into RT. So based on this equation, we can have what should be the value of Q p – Q v.

Now before going to calculate that you have to know what should be the delta n. So this delta n will be is equal to here what will be the you know product side that is you know 1 and minus here you can say that it will be half this, this is carbon. So it will be you know simply as we can say it will be half.

Now we can say that since c is you know solid, since c is solid we can, we cannot consider here this you know coefficient there. So based on which we can say that Q p

- Q v that will be is equal to then here what is delta n, this is half into R, R value is 8.314. This is basically joule per you know mole.

That is K here and into here R here into t, t is here at 25 degrees Celsius. So it will be 298 Kelvin, you have to convert it. Then finally, it is you know coming as 1239 you know joule per gram mole. So this is your Q p – Q v. This is the difference of this heat based on this constant pressure and constant volume.

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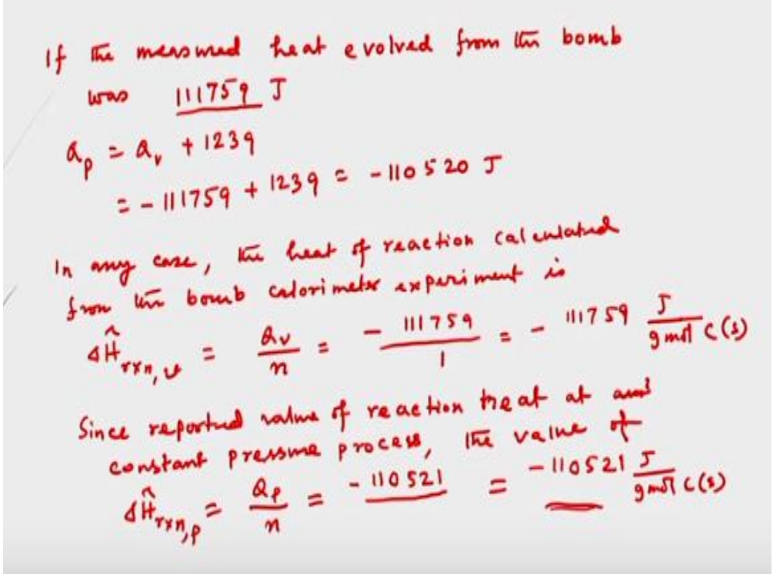

If the measured heat evolved from the bomb was $\underline{111759}$ J

$$Q_p = Q_v + 1239$$

$$= -111759 + 1239 = -110520\ J$$

In any case, the heat of reaction calculated from the bomb calorimeter experiment is

$$\Delta\hat{H}_{rxn,v} = \frac{Q_v}{n} = -\frac{111759}{1} = -111759\ \frac{J}{g\,mol\ C(s)}$$

Since reported value of reaction heat at and constant pressure process, the value of

$$\Delta\hat{H}_{rxn,p} = \frac{Q_p}{n} = \underline{-110521} = \underline{-110521}\ \frac{J}{g\,mol\ C(s)}$$

Now if the measured heat, let us considered that if the measured you know heat evolved from the bomb was 111 point sorry 111759 joule, this total amount of this heat is evolved from the bomb. Then we can say Q p will be is equal to Q v plus this 1239 here as per this equation.

So it will be coming as here minus, you know that -111759. This is reverse that is why negative plus here 1239. So it is coming as -110520 joule. So this much of heat is you know released at constant pressure. Since you have this value of heat energy that is released or evolved as per constant volume is 111759 joule.

Now if we consider that the size of this correction you know is relatively insignificant compared to either the you know quantity that is Q p and Q v. Basically what should be the heat of reaction based on this you know Q v and Q p that you have to calculate.

So in any case, let us in any case, the heat of reaction, calculated form the bomb calorimeter experiment is delta H rxn at a specific condition at constant volume. That will be is equal to Q v by n. So it will be here -111759, that is a constant volume by divided by n, n is here 1.

So it will be is equal to simply -111759 here joule per gram mole of that carbon, that is solid. And similarly, we can calculate what should be the you know heat of reaction based on constant pressure that is experimentally obtained.

So since the reported value of heat of reaction from this combustion reaction we can write here since reported value of reaction, heat or heat of reaction at constant pressure process the value of that heat of reaction as delta H rxn hat at specific condition that will be is equal to Q p by n. So that will be is equal to here -110521 divided by 1 mole of carbon.

So this will be is equal to -11052 here joule 521 sorry 521 joule per gram mole of carbon solid. So this is at constant pressure. So this value is actually obtained experimentally when there is a you know heat released from that burning of coal at constant pressure and the specific heat of that reaction at constant pressure then can be calculated as like this.

Now this value, now if you know this you know or if you can experimentally obtain the value of reaction or heat of reaction at constant pressure from which you can easily calculate what will be the you know value of heat evolved at constant volume. So those are related based on that you know, ideal gas equation at constant you know temperature there.

So from which we can simply you know relate these things based on that you know constant volume and constant pressure system. And once you know either one of this you know value, you can calculate other value of this heat released by that reaction.

So it is interesting that here that constant pressure system you know always to be you know referred in any process instead of constant volume system because you know to maintain that constant volume system and doing the experiment it is very tough.

Whereas you know that constant pressure system to be maintained it will be you know easier relative to that constant volume system. So if you are having that value of constant pressure based you know heat released by that reaction, then from the relation of this equation represented by this equation, you can easily calculate what should be the heat evolved by the reaction at constant volume there.

So it is sometimes required to know the heat of reaction at constant volume condition. So we have described the heat of combustion based on the heat of reaction that is experimentally obtained by you know by combustion reaction and also heat of combustion reaction can be you know calculated based on that heat of you know combustion of individual constituents.

Also heat of reaction can be calculated once you know that heat of reaction based on the heat of combustion. So all are related to each other and some examples are given to you. I would suggest you to go further to practice with some examples given in the textbooks.

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Further reading……

Text Books:

- R. M. Felder, Ronald W. Rousseau, Lisa G. Bullard, Elementary Principles of Chemical Processes, 4th Ed., John Wiley & Sons, Asia, 2017.
- D. M. Himmelblau, J. B. Riggs, Basic Principles and Calculations in Chemical Engineering, 7/8th Ed., Prentice Hall of India, 2012.

Reference Books:

- N. Chopey, Handbook of Chemical Engineering Calculations, 4th Ed., Mc-Graw Hill, 2012.
- Olaf, K.M. Watson and R. A. R. Hougen, Chemical Process Principles, Part 1: Material and Energy Balances, 2nd Ed., John Wiley & Sons, 2004.

And it will be helpful to better understand of this heat energy balance concept and further calculation based on this concept. And next lecture we will discuss something more about that material balance and energy balance based on that you know transient condition like at unsteady state condition how you can calculate or you can do the material balance and you know energy balance there.

So we will be discussing from next module onward those things. So thank you for giving attention in this lecture.